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SPECTRA AND STRUCTURE OF SOME FLOPPY MOLECULES COOLED IN SEEDED JET

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The pioneering works of Raman and Mizushima in the area of vibrational spectroscopy have been widely exploited by physical chemists for obtaining structural information about molecules. This lecture, dedicated to the two great scientists, reviews our work on low-frequency vibronic spectra of jet-cooled large organic molecules.

A chemical change involves hopping of the system from one well in the multi-dimensional potential energy surface (PES) to another. A simplified model for this process which lends itself to further detailed treatment is large-amplitude vibration along the soft mode of a floppy molecule. It is therefore pertinent that we collect more information about the ground and/or excited state PES corresponding to motions like aryl rotation, ring-puckering, H-bond stretching and intermolecular dissociation.

In the condensed phase the perturbation by the surrounding environment is large enough to cause deformation and blurring of conformer identities. It is necessary, therefore, to work with a set of collisionless, cold, uniformly moving molecules as provided in a jet. The vibronic features of the laser-induced fluorescence (LIF) and fluorescence excitation (FE) spectra of the cold molecular beam are often amenable to analysis in terms of a fundamental frequency and its higher harmonics, which in turn can be correlated with the nature of excited and ground PESs.

The molecules of interest to us are listed in the table. In particular, the power of two-colour IR-UV double resonance technique in determining structures of clusters is illustrated with five hydrates of tetrahydroisoquinoline.

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References:

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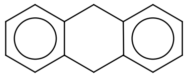
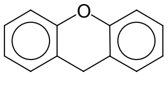
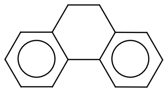
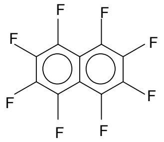
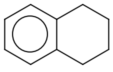
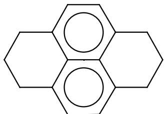
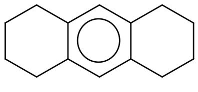
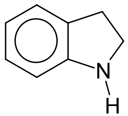
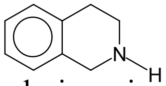
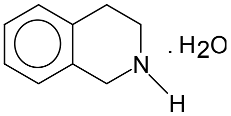
Table I

Molecules	**Reference number**	**Vibrational modes (cm^{-1})**		**Description of modes and potential energy surface**
		Ground	**Excited**	
 Dihydroanthracene	1	-	28	Butterfly (Puckering) (symmetry-equivalent double well, low barrier)
 Xanthene	2	-	53	Butterfly (Puckering) (symmetry-equivalent double well, low barrier)
 Dihydrophenanthrene	3	-	90	Torsion (symmetry-equivalent double well, low barrier)
 Octafluoronaphthalene	4	135	26	Butterfly (Puckering) (soft mode with barrier less than zero-point energy)
 Tetralin	5	105 160	95 179	Puckering Twist Puckering Bend
 Hexahydropyrene	6	-	66, 87 128	Puckering (in phase and out-of-phase boat and chair form)
 Octahydroanthracene	7	188 81	129 60	Ring Puckering twist [in phase and out-of-phase] (Sym and antisym twist conformer)
 Indoline	8		45 119	Puckering coupled to N-inversion
 Tetrahydroisoquinoline	9	95 144	92 98	Out-of-plane N-puckering (axial and equatorial form)
 THIQ $(H_2O)_1$ cluster	10	3717 3377 3352	- - -	Free OH H-bonded OH H-Bonded NH (Five clusters with five distinct IR-signatures)